

LOWER PASSAIC RIVER RESTORATION PROJECT TECHNICAL UPDATE RE: ASSESSMENT OF PCB AQUEOUS PARTITIONING AND AVAILABILITY IN LOWER PASSAIC RIVER SEDIMENTS (GROUP C ANALYTES)

Introduction

Background

In 2005, the U.S. EPA provided guidance for remediation of contaminated sediments which identified contaminant bioavailability as a key parameter for remedial investigations, risk characterization, and feasibility studies (U.S. EPA, 2005). The guidance emphasized the importance of evaluating contaminant bioavailability for the evaluation of contaminant fate and transport processes and assessment of monitored natural recovery (MNR). Although the EPA defined contaminant bioavailability as an important parameter for developing site-specific sediment remedial action objectives (RAOs), little or no guidance has been provided on the analytical methods and approach for evaluating this parameter.

Over the last 15 years, there have been a number of studies that have investigated aqueous partitioning characteristics of sediment-bound hydrophobic organic chemicals as an indication of their bioavailability, recognizing that movement of the chemical to the sediment porewater represents a significant environmental exposure pathway [Carroll et. al., 1994; Kan, et.al., 1997; Cornelissen, et. al., 1997; Ghosh, et. al., 1999; Barring, et. al., 2002; Jonker and Koelmans, 2002; Bucheli and Gustafssen, 2003; Cornelissen, et. al., 2004; Cornelissen, et. al., 2005; Jonker and Barendregt, 2006]. These studies have shown that hydrophobic organic chemicals are tightly bound to the carbon in the sediment matrix and that this binding is significantly greater when multiple forms of anthropogenic carbon are present (e.g., urban river systems) in addition to natural organic carbon [Arp, et. al., 2009].

Additional research has indicated that this increased binding reduces environmental exposure and, ultimately, the uptake of the chemicals by environmental receptors [Kraaij, et. al., 2002; Kraaij, et. al., 2003; Moermond, et. al., 2004]. These studies led to the proposed approach of adding activated carbon, coal or charcoal to sediments as a remedial strategy which results in reductions in bioaccumulation of PCBs by benthic aquatic organisms (Zimmerman et al, 2004; Sun and Ghosh 2007). More recently, a comprehensive field data set was used to investigate the relationships between the accumulation of PCBs in sediment toxicity tests and the PCB concentrations in the solid phase and free aqueous phase of seven field-contaminated freshwater and marine sediments. The sediment samples were collected from Lake Hartwell, Hunters Point, Grasse River, Milwaukee River, Niagara River and Crab Orchard Lake (Werner et al., 2010). Literature-derived partitioning relationships based on sediment total organic carbon, congener specific octanol-water partitioning coefficients (K_{OW}) and sediment PCB congener concentrations were found to overestimate the freely dissolved aqueous concentrations and the concentrations in the laboratory-exposed worms by an average factor of 8 and 33, respectively with some samples overestimated by more than 2 orders of magnitude.

LPR Study Goals and Objectives

Given this background, Dr. Upal Ghosh of the University of Maryland, Baltimore County (UMBC), was contracted by the CPG to determine the aqueous partitioning characteristics of

the Group C analytes identified in the Low Resolution Coring (LRC) report for a suite of six sediment samples from the Lower Passaic River (LPR). This study had two goals:

1. Develop data for establishing and evaluating a project-specific method for quantifying the sediment/porewater partitioning coefficients for PCBs; and
2. Complete a preliminary survey of the site-specific PCB aqueous partitioning coefficients in sediment samples collected from three geochemical regimes of the Lower Passaic River [soft organic sediments in the estuarine zone; sediments from the transition zone of alternating fresh and brackish water; and hard sediments in the freshwater reach below Dundee Dam].

The data from this study have been received and subjected to a quality assurance/quality control review. These data were contained in the original laboratory electronic data delivery (EDD) submissions, which were posted to PREMIS as they were received. The analysis of these data is in progress. This memorandum provides an update of the status of this data analysis effort.

Study Samples and Congener Selection

Six grab samples were collected as part of the LRC Task of the Lower Passaic River Restoration Project (LPRRP) Remedial Investigation/Feasibility Study. These samples were c-located with LRC cores whose surface segments contained measurable Group C analytes (Figure 1). The sample locations were chosen to represent the entire length of the LPR (River Mile 0.5 to River Mile 17.5) and a range of geomorphic characteristics, including point bars, straight side channels, channel bends, and Dundee Lake (Table 1).

As shown in Table 1, the study samples also represent a wide range of grain sizes, total organic carbon (TOC) content, and chemical concentrations, as summarized below:

- Grain size:
 - Gravel: 0% to 11%;
 - Sand: 13% to 87%;
 - Silt: 2% to 58%; and
 - Clay: 0.06% to 35%.
- Total organic carbon: 3.4% to 18%;
- Total PAHs (high molecular weight [HMW] plus low molecular weight [LMW]): 8.6 to 535 mg/kg;
- Extractable petroleum hydrocarbons: 246 to 2,400 mg/kg; and
- Total₂₀₉ PCBs: 0.536 to 2.12 mg/kg.

The Total₂₀₉ PCBs represent the sum of 209 PCB congeners. However, due to time and budget constraints, the aqueous partitioning study only focused on a subset (i.e., 42) of these congeners that were selected from the 209 congeners to include: (1) representative compounds from each homologue group (i.e., the full range of compound molecular weights and associated chemical and physical properties); (2) congeners measured as part of the NOAA National Status and Trends, Mussel Watch Program [NOAA, 1989]; and (3) congeners that are known to have dioxin-like properties [Van den Berg, 2006]. Table 2 identifies the 42 individual PCB congeners that were selected for analysis and provides information on their physical and chemical

properties. The summation of the concentrations of these 42 PCB congeners (i.e., Total₄₂ PCBs) for the six study samples ranged from 0.319 to 0.874 mg/kg. As a percentage of the Total₂₀₉ PCBs for each of these samples, they represented between 41% to 50% of the detected PCBs

It is important to note that the homologue group criterion was the primary selection criterion for this study given that the achievement of the study goals, i.e., the development of a project-specific method for quantifying sediment/porewater PCB partition coefficients and the conduct of a preliminary survey of PCB congener partition coefficients for the LPR, requires that the full range of PCB congeners (i.e., low to high molecular weight) be examined. Since it was not realistic to examine the partitioning characteristics of all 209 congeners as part of this study, the examination of representative compounds from each homologue group was appropriate¹. The other criteria, the NOAA list and congeners with dioxin-like properties, only served to further narrow the congener selection to focus on those congeners that would likely be important if further investigation of the PCB and dioxin/furan partitioning from the LPR sediments is warranted. However, to fully utilize the partitioning of hydrophobic organic chemicals from sediment to porewater in the LPR as a sediment management tool, it will be necessary to have the ability to measure and/or predict the partitioning of those hydrophobic chemicals, e.g., PCB congeners, dioxin/furans, PAHs, and others, that are of environmental interest at the site.

Experimental Methodology

Laboratory Aqueous Partitioning Tests and Sample Analysis

Batch aqueous partitioning tests were conducted for each sample, in duplicate, using previously published methods (Ghosh et al. 2000; Khalil et al. 2006). The analysis of freely dissolved PCBs in water samples (C_{fw}) is complicated by interference from micro-particulate and colloidal organic matter which can increase the apparent dissolved aqueous concentration of hydrophobic organic chemicals such as PCBs. To address this analytical problem, aqueous partitioning tests were also conducted using a third phase consisting of 76 µm thick strips of the polymer, polyoxymethylene (POM). At the end of the test, the POM, water, and sediment samples were analyzed for PCB congeners. Details of the laboratory aqueous partitioning test procedure were previously provided in Appendix D of the LRC Quality Assurance Project Plan (QAPP) (ENSR 2008). In brief, 100 +/- 5 g of wet sediment (dry weight basis) was homogenized and transferred to a 1L wide mouth amber jar with a PTFE-lined lid. One gram of sodium azide was added to prevent microbial activity and metabolism of PCB congeners. Reagent grade water was then added to each jar to achieve 900 mL total volume followed by the addition of a pre-cleaned and weighed strip of POM (approximately 200 mg of 76 µm thick strips). The jar contents were mixed by rolling the jars on a cell culture roller at 3.0 +/- 0.2 rpm for 28 days at room temperature. Two blank jars, with only water, sodium azide and POM in the same quantities were prepared and mixed for 28 days alongside the samples as experimental controls. At the end of the test period, the POM strip was removed from the jar, briefly rinsed with reagent water and wiped with laboratory tissue paper to remove particulates and dry the surface. The POM strips were then weighed and stored in solvent-rinsed jars prior to extraction and analysis of PCB congeners. Following removal of the POM, the jars were placed in an upright position and the sediment was allowed to settle for 24 hours. Following the settling period, suspended solids in the aqueous portion of the sample were flocculated with a 0.1M

¹ Ultimately, it would be desirable to correlate the aqueous partitioning coefficients to a set of physical and/or chemical properties that would permit the prediction of congener partitioning to the sediment porewater based on the analysis of more conventional physical and chemical sediment characteristics.

alum solution and allowed to settle for 72 hours. Flocculation was repeated for samples with no discernable flocculent layer. For TOC analysis, subsamples consisting of two 10 mL aliquots of clarified water were collected from each jar (one from the top 20% and one from the bottom 20% of the water column) and combined into a single 20 mL sample. The recoverable mass of clarified water (approximately 500 g) was measured to the nearest 0.1 g, and prepared for extraction and analysis of PCB congeners using high resolution gas chromatography and high resolution mass spectrometry (HRGC/HRMS). Sediment samples in each jar were then collected and dewatered using a Büchner funnel with glass fiber filter for analysis of PCB congeners, TOC, and black carbon (heat stable carbon). Sediment, water, and POM samples were analyzed using HRMS methods (EPA 1668A) for the selected PCB congeners. These analytical methods and the SOPs were also presented in the previously referenced QAPP.

Laboratory Particle Density and Size Classification

Each of the six sediment samples was analyzed for moisture content and then wet sieved to separate the samples into four size fractions (<63 µm, 63-250 µm, 250-1,000 µm, and >1,000 µm). After size separation, each of the size fractions was separated by density using a high density (specific gravity of 1.8) solution of cesium chloride. The size and density separations followed methods described in Ghosh et al. (2003). Each sediment fraction was air dried and weighed to obtain the mass fractions in each class. Microscopy analysis was conducted in visible light with a stereomicroscope to assess the nature of the lighter density, 250 -1000 µm, organic particles of each sediment.

The two most abundant lighter density fractions were selected from each sediment sample for further petrography analysis. Petrography analysis, using plane and polarized light, was conducted using ASTM standard methods for coal analysis: (1) D2797-Preparing Coal Samples for Microscopic Analysis by Reflected Light; (2) D2798-Microscopic Determination of the Reflectance of Vitrinite in a Polished Specimen of Coal; and (3) D2799-Microscopic Determination of Volume Percent of Physical Components of Coal. These methods were used to determine the kind, or morphology, of carbonaceous particles and the relative abundance of carbonaceous solids such as soot, coal, coke, and tars as described in Ghosh et al. (2003).

Study Results

Project-Specific Method for Quantifying the Sediment/Pore Water Partitioning Coefficients for PCBs.

Evaluation of Polyoxymethylene (POM) for Determining PCB Partition Coefficients

The approach for determining the partitioning behavior of PCB-impacted sediment that was used in this study was recently compared and contrasted to the other most common alternative methods [Gschwend, et. al., 2011]. Gschwend, et. al. (2011) compared the ability of three methods that employ polymers, with known polymer-water partition coefficients, to estimate the partitioning of PCBs from sediment into porewater. In addition to the POM used in this study, PCB partitioning was determined using polydimethylsiloxane (PDMS) and low-density polyethylene (LDPE). These polymers were exposed to a single sediment in two modes, one in which they were exhaustively mixed (tumbled) with the sediment [POM and LDPE], as was done in this study, and the other in which they were simply inserted into a static bed (passive) of sediment [PDMS and LDPE]. The PCB partitioning behavior determined using the three polymers was compared to the results using an air bridge, which is the “gold standard” for determining partitioning coefficients, since this methodology removes the potential for all

interferences associated with the presence of colloids and dissolved organic carbon. As shown in Table 3, Gschwend et. al.'s (2011) comparison of the porewater concentrations for specific PCB congeners with the air bridge results indicated that the results for the tumbled polymers [POM and LDPE], on average, agreed within 20%: the average POM-inferred porewater concentration was 87%, while the LPDE-inferred porewater concentration was 83%, of the measured air bridge concentration. In contrast, the passive sampling approach [LDPE and PDMS] agreed with the air bridge results only within a factor of 2. Based on these results, the authors concluded that more accurate site assessments can be achieved by employing polymer measurement techniques, such as POM. These results support the selection and use of POM in the LPR study for characterizing the PCB aqueous partitioning of the LPR sediments.

Availability of POM-Water Partitioning Coefficients [Kpoms] for PCB Congeners

A key requirement for the successful adoption of the POM methodology for determining site-specific sediment-water partitioning coefficients (Koc) is the availability of reliable and widely accepted values for POM-water partitioning coefficients (Kpom) for the full range of PCB congeners. Recent work by Hawthorne et al. (2009) reported Kpom values for 62 PCB congeners. As part of that study, Hawthorne, et.al. (2009) were able to measure Kpoms for a wide range of PCB congeners, with Log Kows ranging from 5 to nearly 9. This was possible because of the use of a solid phase microextraction technique that was used to measure the low aqueous PCB concentrations of these low solubility PCBs. On the other hand, the aqueous PCB detection limits of this study were too high to permit the direct measurements of Kpoms for PCB congeners with Log Kows greater than 6.8. For those compounds, it was necessary to predict the Kpom using the following relationship: $\text{Log Kpom} = 1.118 \text{ Log Kow} - 0.995$. This relationship was derived using the Kpom/Kow experimental data for those compounds with Log Kows ranging from 5.1 to 6.8.

Table 4 presents a comparison of the Kpom values generated as part of this study with those presented in Hawthorne et al (2009). With few exceptions (PCB28, PCB31 and PCB66), the table indicates better agreement for the PCB congeners with a log Kow smaller than 6.8, i.e., those congeners for which both laboratories made direct aqueous measurements of the PCB concentrations. However, for the PCB congeners where it was necessary to predict the Kpoms as part of the LPR study, i.e., Log Kows greater than 6.8, the differences in the Kpoms were consistently greater, as the predicted Log Kpoms from this study deviated by one log unit or more from the measured values of Hawthorne et. al. The reason for these differences is not clear; however, the use of the experimental values of Hawthorne are more in line with those values reported in the literature by Cornelissen [Cornelissen, et. al. 2008] and Jonker and Hawthorne [Jonker and Hawthorne, 2011]. These Kpom data of Hawthorne, Cornelissen and Jonker, which show good agreement, are presented in Table 5 for five PCB congeners with Log Kows ranging from 6.83 (PCB 118) to 7.64 (PCB 180)

Moving forward, consideration will be given to using the Kpom experimental data from Hawthorne [Hawthorne, et.al., 2009] for estimating Kocs for PCB congeners with Log Kows greater than 6.8 and as high as 9.0. This will provide Koc information for these PCBs without having to resort to the use of the empirical correlations (and their inherent uncertainty) to predict Kpom from Kow data.

Preliminary Survey of the Site-Specific PCB Aqueous Partitioning Coefficients in Sediment Samples

Measured LPR PCB Partition Coefficients ($K_{oc}(pom)$)

The $K_{oc}(pom)$ were determined for 12 sediment samples - six surface sediment samples and their duplicates (Table 6). The $K_{oc}(pom)$ was determined by dividing the PCB concentration in the sediment by the fraction of organic carbon (f_{oc}) and then dividing that number by the concentration of the PCB in the porewater. The concentration of the PCB in the porewater (C_{fw-pom}) was determined by taking the concentration of the PCB in the POM and dividing it by the water-POM PCB partition coefficient, K_{pom} . Since the K_{pom} s presented in Table 4 are chemical-specific (i.e., not site- or sediment-specific), they were used in these calculations for all of the sediment samples. As shown in Table 6 and Figure 2, the $\log K_{oc}(pom)$ ranged from 4.54 to 11.81, generally increasing with the molecular weight of the congener.

Comparison of LPR $K_{oc}(pom)$ to Literature Values of K_{oc} ($K_{oc}(Lit)$)

Laboratory Samples - Natural Organic Matter

Figure 3 compares the measured $K_{oc}(pom)$ values for the 42 congeners to the literature K_{oc} values ($K_{oc}(Lit)$) for these same PCB congeners [Schwarzenbach, et.al., 2003]². In Figure 3, the $\log K_{oc}(pom)$ is plotted against the $\log K_{oc}(Lit)$ for all of the 42 congeners in the six sediments. Also shown in Figure 3 is the 1:1 line, which represents the points where these partition coefficients would be equal. It is apparent from this graph that the measured $K_{oc}(pom)$ values of this study are uniformly greater than the $K_{oc}(Lit)$ values by one to five orders of magnitude³. This, in turn, suggests that the concentration of the PCB in the sediment porewater would be one to five orders of magnitude less than predicted using the $K_{oc}(Lit)$. Figure 4 presents the \log of the ratio of $K_{oc}(pom)$ to $K_{oc}(Lit)$ for the 42 individual PCB congeners of this study. This figure indicates that the differential between these two estimates of PCB partitioning coefficients ranges from one to five orders of magnitude, generally increasing with the molecular weight of the homologue group⁴.

Figure 5 presents the \log of the $K_{oc}(pom)$ for the 42 PCB congeners as a function of river mile. This figure indicates the $\log K_{oc}(pom)$ are consistent along the entire length of the river, ranging between values of 4 and 12. A similar observation is made when the \log of the ratio of $K_{oc}(pom)$ to $K_{oc}(Lit)$ is plotted as a function of river mile (Figure 6). These data indicate that the enhanced binding of the PCBs to the LPR sediments is also consistent along the length of

² These literature values of K_{oc} [$K_{oc}(Lit)$] were estimated using a linear free energy relationship based on the octanol-water coefficient (K_{ow}) of the compound.

³ Although the Gschwend et.al. (Gschwend et. al., 2011) study involved only one sediment sample, the data also indicated that porewater concentrations estimated based on sediment concentrations normalized to $f_{oc}K_{oc}(Lit)$, the weight fraction of organic carbon times the organic-carbon normalized partition coefficient from the literature, averaged a factor of 7 too high. It was concluded from this study that "more accurate site assessments can be achieved by employing sampling devices in which polymers, with known polymer-water partition coefficients, are used to absorb the contaminants from the sediment."

⁴ Since the Y-axis in Figure 4 is the \log of the ratio of the partition coefficients, the values on the y-axis represent the order of magnitude difference between the two coefficients, i.e., a y-value of 1 equals one order of magnitude difference while a value of 5 equals a difference of 5 orders of magnitude.

the river, spanning the range from 1 to 5, demonstrating that the site-specific PCB partitioning factor is 1 to 5 orders of magnitude greater than would be predicted using the Koc(Lit). As previously noted, Koc(Lit) is estimated based on relationships with Kow that were derived from partitioning experiments involving natural organic carbon, only.

Field Samples – Anthropogenic Carbon

A similar comparison of the study results from the LPR study (i.e., Koc(pom)), was made with the data that were presented in a recent survey of the sediment-porewater distribution of chlorinated aromatic hydrocarbons in anthropogenic-impacted sediments [Arp et. al., 2009]. This study assessed a diversity of PCB sorption/partitioning behavior by examining all of the total organic carbon (TOC)-normalized *in situ* sediment-porewater partitioning coefficients for impacted field sediments in the peer-reviewed literature. It included several hundreds of data for PAHs, PCBs, PCDD/Fs, and chlorinated benzenes and covered a large variety of sediments, locations, and experimental methods. A primary difference between the studies included in this article and the laboratory studies noted above is that Arp et. al. (2009) focused on field samples of impacted sediments that had been in the environment for long periods of time and in contact with anthropogenic forms of carbon, in addition to natural organic carbon.

Specifically with regards to PCBs, the Arp et. al. (2009) study noted the existence of a very diverse data set. In total, there were 142 average, minimum, and maximum Koc values for 24 compounds in 7 citations⁵. Figure 7 compares the PCB partitioning data of Arp et.al. (2009) and the LPR study for those PCB congeners for which both studies presented data (i.e., 19 of the 42 congeners in the LPR study). As shown, the LPR data are generally consistent with the data summarized by Arp et. al. (2009) for the anthropogenic impacted sediments. In most cases, the median Koc(pom) of the LPR PCB partitioning study fell near or within the range presented by Arp et. al.. The largest differences were observed for the higher molecular weight PCB congeners where the median of the LPR study results were above the upper limit of the range presented by Arp et. al. However, these differences are not significant, and are generally less than a fraction of a log unit (i.e., approximately a factor of 2 to 3). This comparison suggests that field sediments that have been in the environment and exposed to anthropogenic sources of carbon bind the PCBs to a greater extent than those in which natural organic carbon is the dominant form of carbon in the sediment.

Characteristics of Carbon in the LPRSA Sediments

Coke, carbon black, and some coals contribute to the black carbon [BC] content of the six sediment samples. The two samples with the highest BC content, 3.5% and 4.5%, [CLRC-079 and CLRC-098, respectively] also showed a high abundance of coal, coke, and carbon black through petrography analysis of the lighter density fractions⁶. Thus, coal, coke, and carbon black materials are likely the primary contributors to the BC measured in the samples and also form the strongest sorptive media for PCBs in the sediment matrix. There are some differences in the sorption capacities of the various black carbon types. For example, as described in Ghosh (2007), the adsorption capacity of black carbon is strongly related to the available surface area for adsorption, and therefore, millimeter sized coke particles and submicron size soot particles may provide similar soot carbon fraction by weight but may have very different sorption

⁵ The study also presented data for 26 congeners of PCDD/DFs, including 83 average, minimum, and maximum *in situ* values of Koc in 4 citations. These data are not discussed in this update.

⁶ The total organic carbon content of these samples ranged from 5.7 to 7.3%. These values are different than those presented in Table 1 because the sediments used in the partitioning study were taken from separate samples collected from the same locations. This variability provides some indication of the extent of the compositional heterogeneity of the sediments that exists within the LPR.

capacities. The higher surface area of the soot particles may afford higher sorption capacity compared to the larger coke/coal particles.

There was not a significant difference in the calculated Kocs[pom] between the samples with the highest BC content [CLRC-098 and CLRC-079] and the lowest BC content [CLRC-044]. This is shown in Figure 8, where the measured Koc(pom) for all 42 congeners are plotted against the total and black carbon content of the samples. As shown, based on this fairly limited number of samples, there is no obvious relationship between Koc(pom) and carbon content. One possible explanation for this lack of correlation can be hypothesized from the petrography results. These results show that in the sample with the low BC content, the BC is primarily composed of sub-micron sized black carbon aggregates that may have higher sorption capacity compared to the larger solid coal/coke particles. Thus, both BC composition (e.g., coke particles versus tire particles) and particle size may be playing a role in governing the partitioning of hydrophobic organic chemicals in sediments.

In general, the petrography analysis revealed the general anthropogenic nature of the carbon present in the LPR sediment samples and confirmed the presence of black carbon through the identification of an abundance of black carbon particles in the sediment that are known to have strong sorption capacity for hydrophobic organic compounds. However, these study results suggest that more information regarding the specific composition of that black carbon and its particle size distribution will be required before correlations between its presence and the PCB partitioning characteristics will be evident.

Path Forward and Schedule

The CPG will continue to evaluate and examine the results presented in this technical update and will provide EPA with a presentation of the study results as part of the upcoming RI Report.

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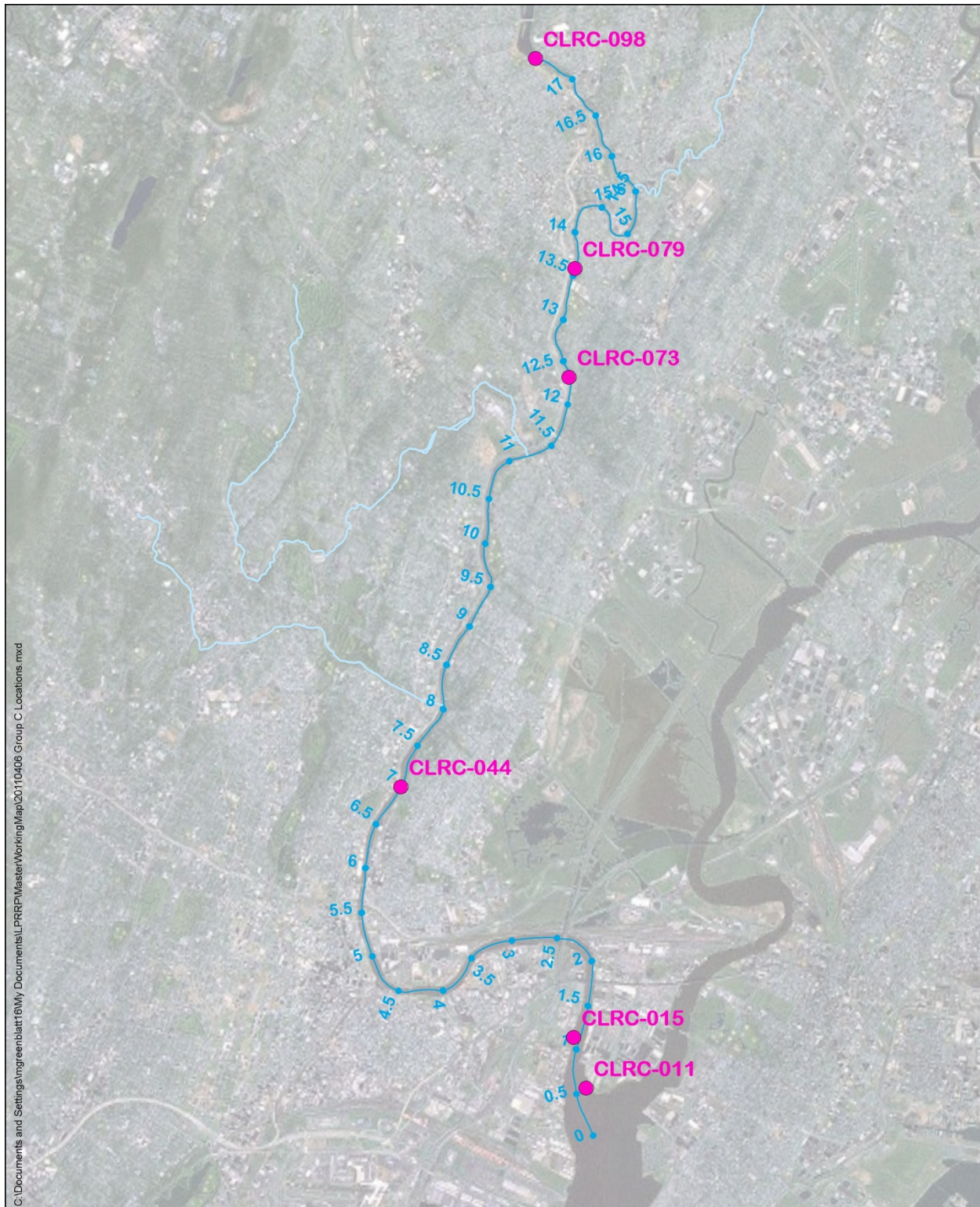


Figure 1. Locations of Surface Sediment Samples Selected for Study

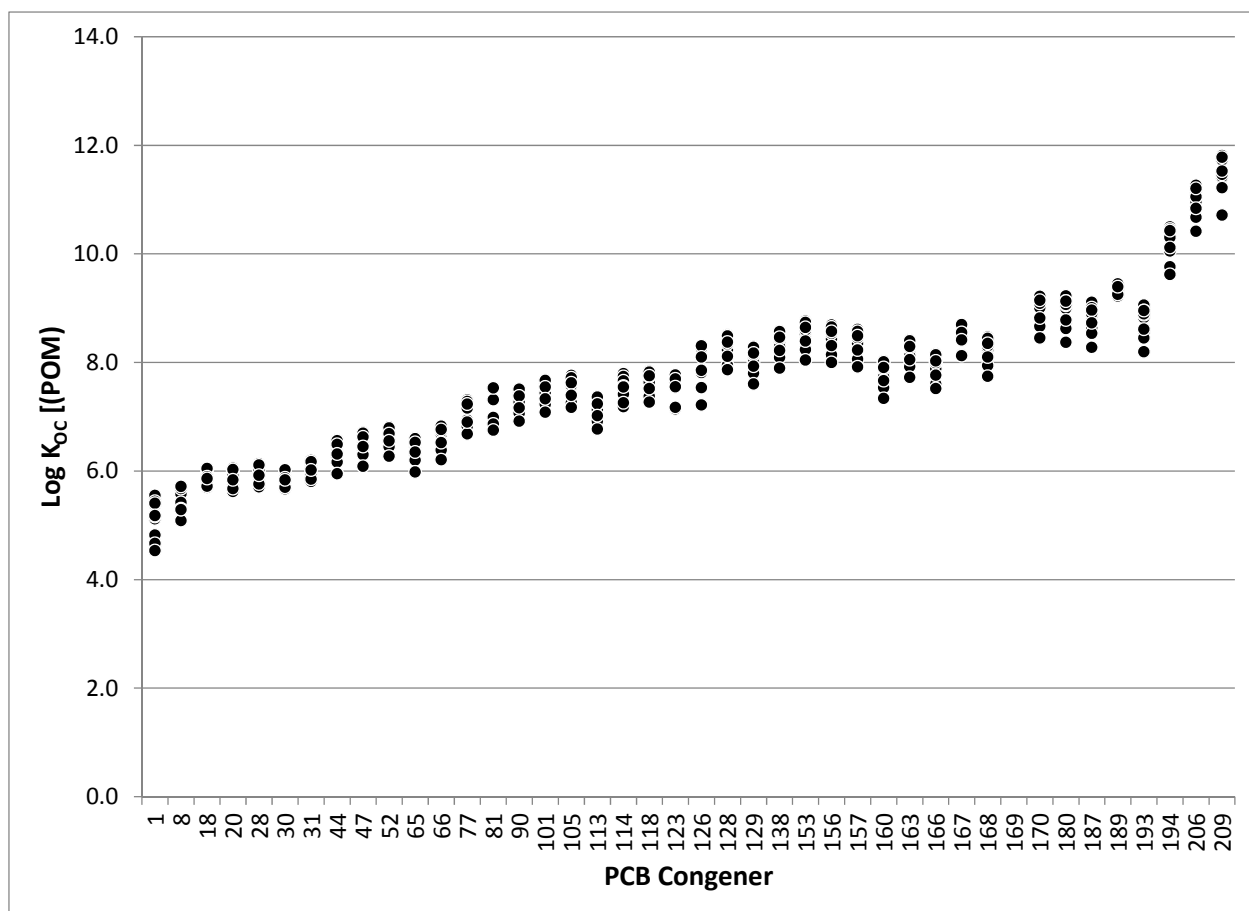


Figure 2. Measured Log K_{oc} (POM) versus the 42 PCB Congeners

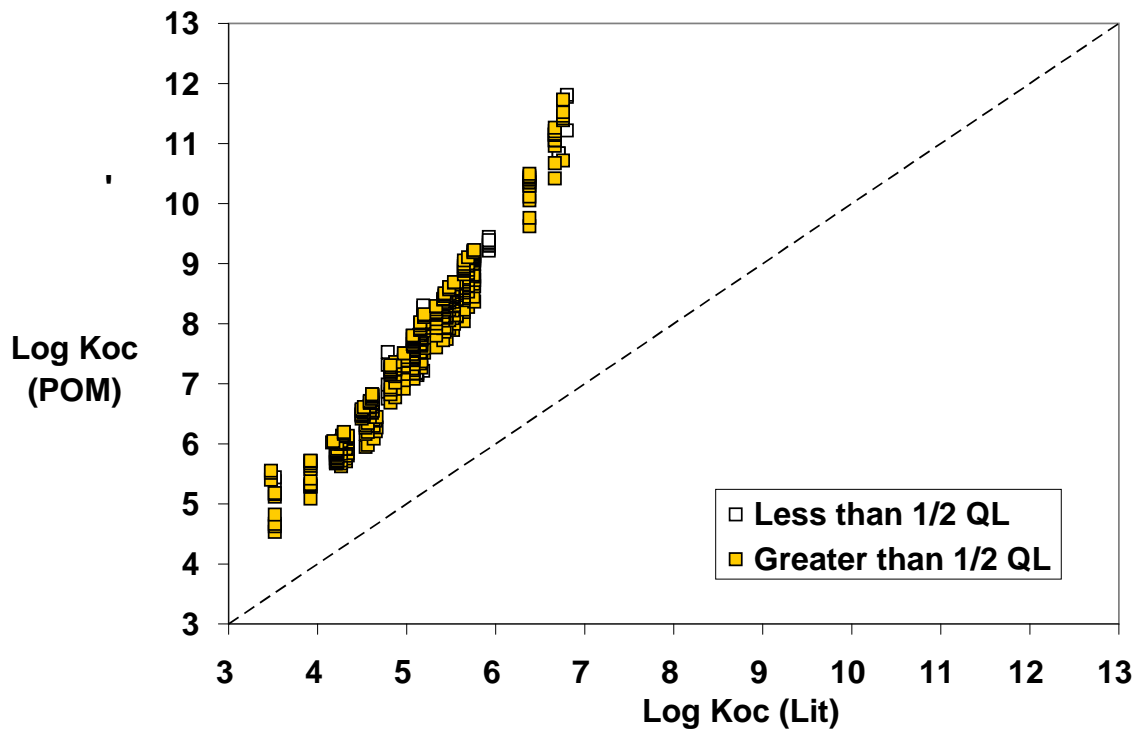


Figure 3. Measured Log Koc (POM) versus Log Koc (Lit) for the LPR sediments

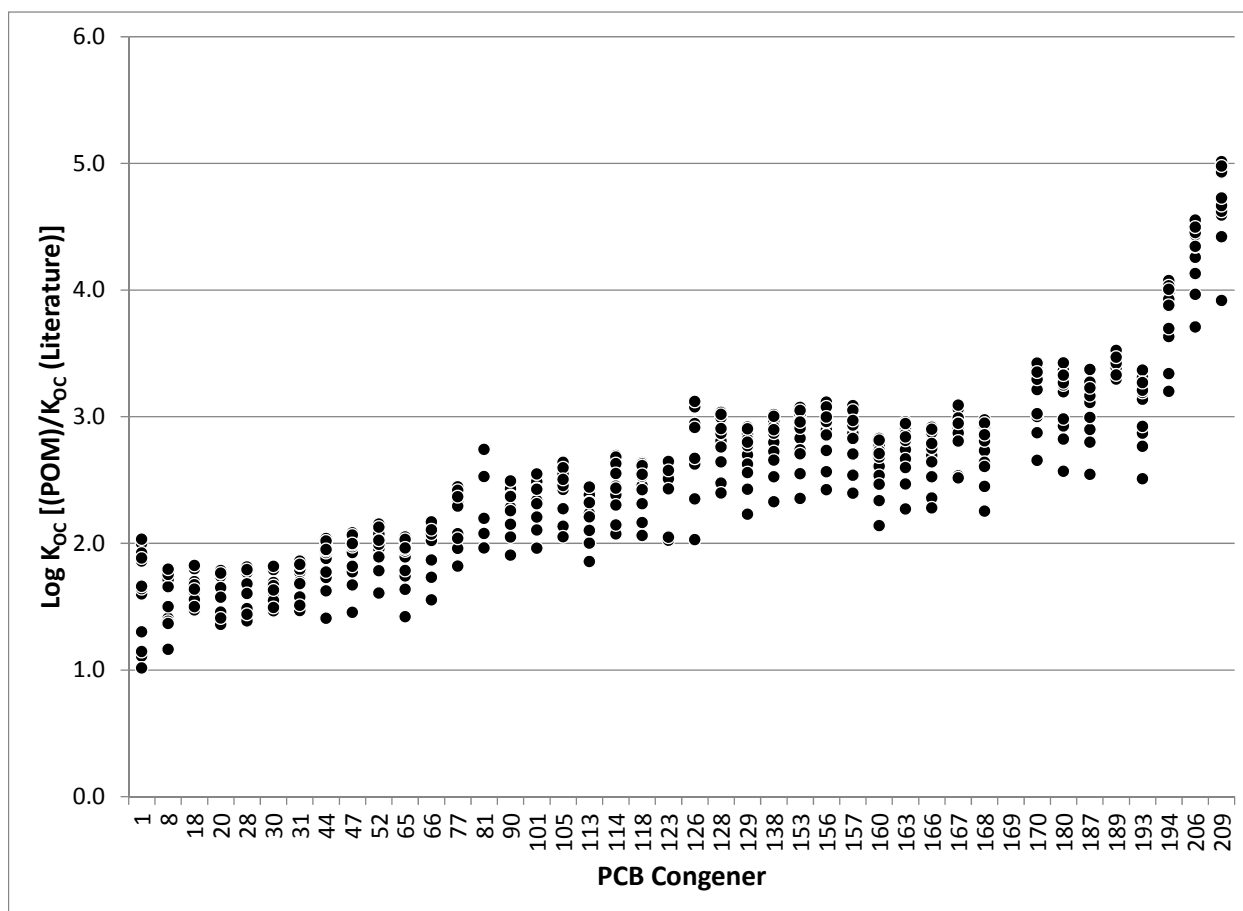


Figure 4. Log of the Ratio of Measured Koc (POM) to the Koc (Lit) Values for the 42 PCB Congeners

Note that the Y-axis is the log of the ratio of the two PCB partitioning coefficients. As such, the y-values represent the order of magnitude difference between the two values, e.g., y=1 is one order of magnitude difference, y=2 is two orders of magnitude, etc.

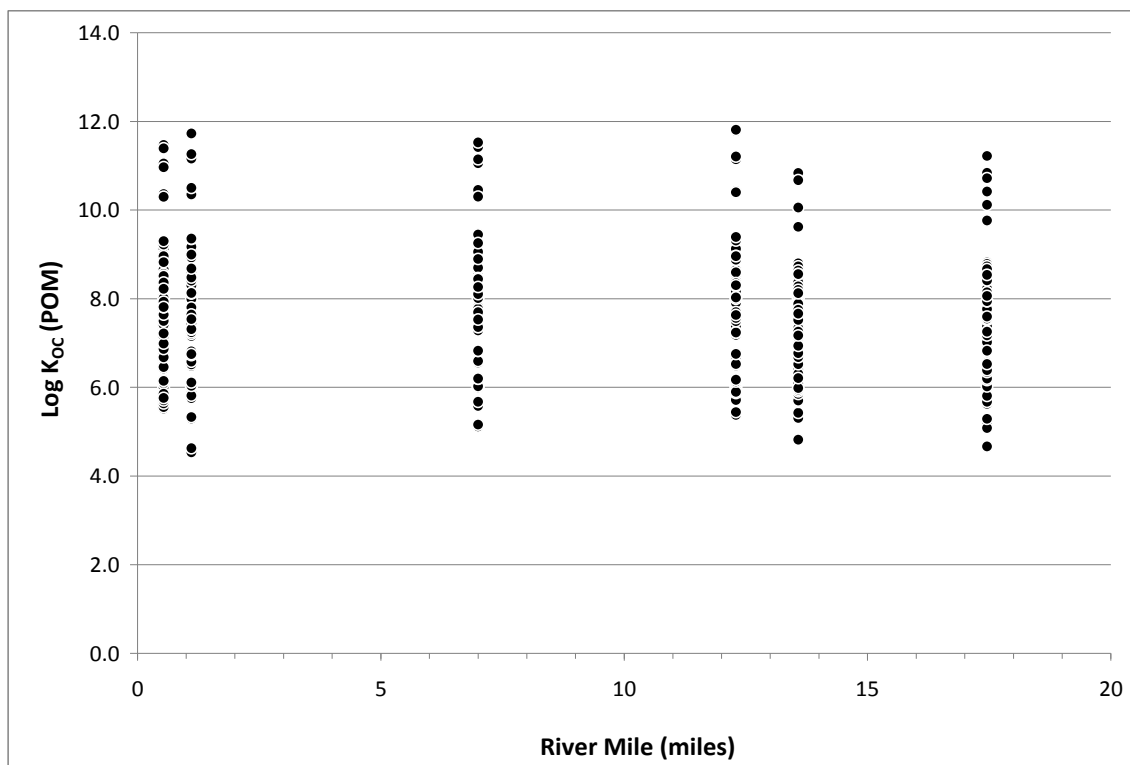


Figure 5. Log K_{oc} (POM) [42 PCB Congeners in Six Sediment Samples] versus River Mile

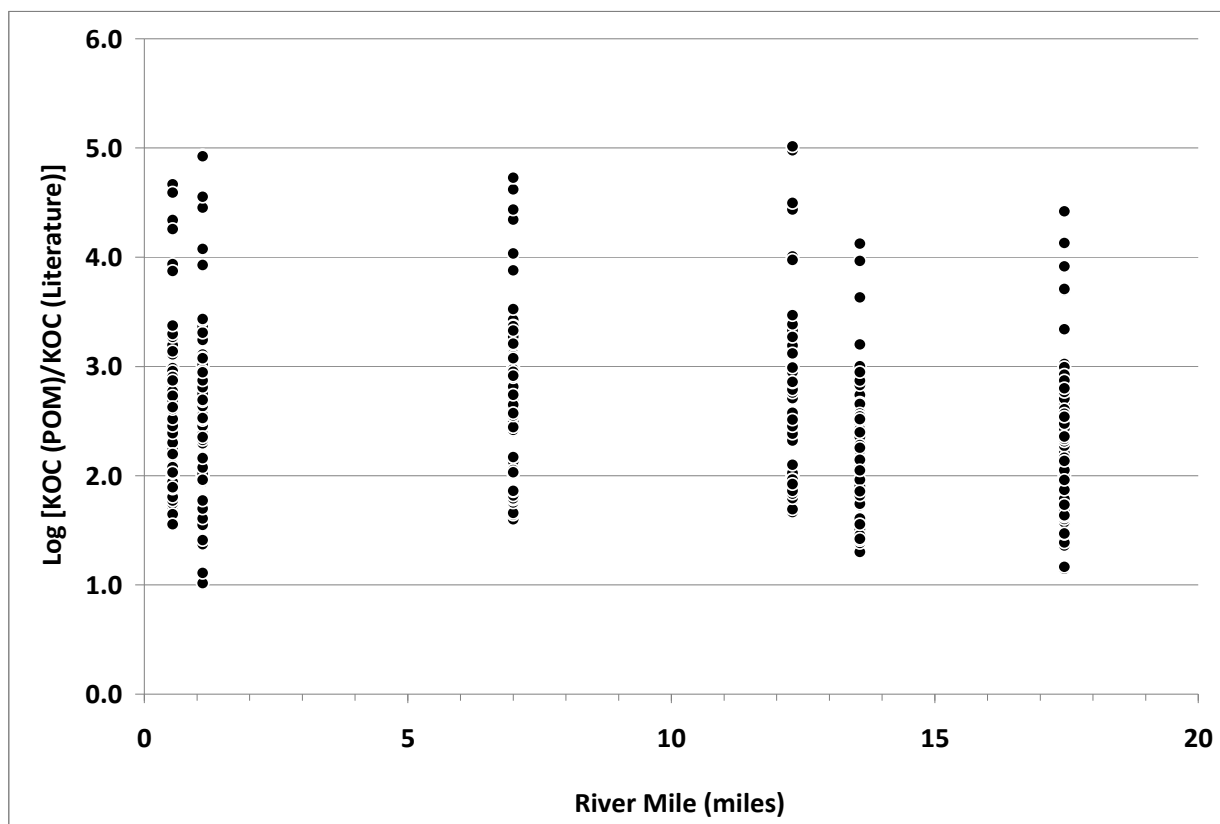


Figure 6. Log of the Ratio of Koc (POM) to the Koc (Lit) by River Mile (42 PCB Congeners in Six Sediment Samples)

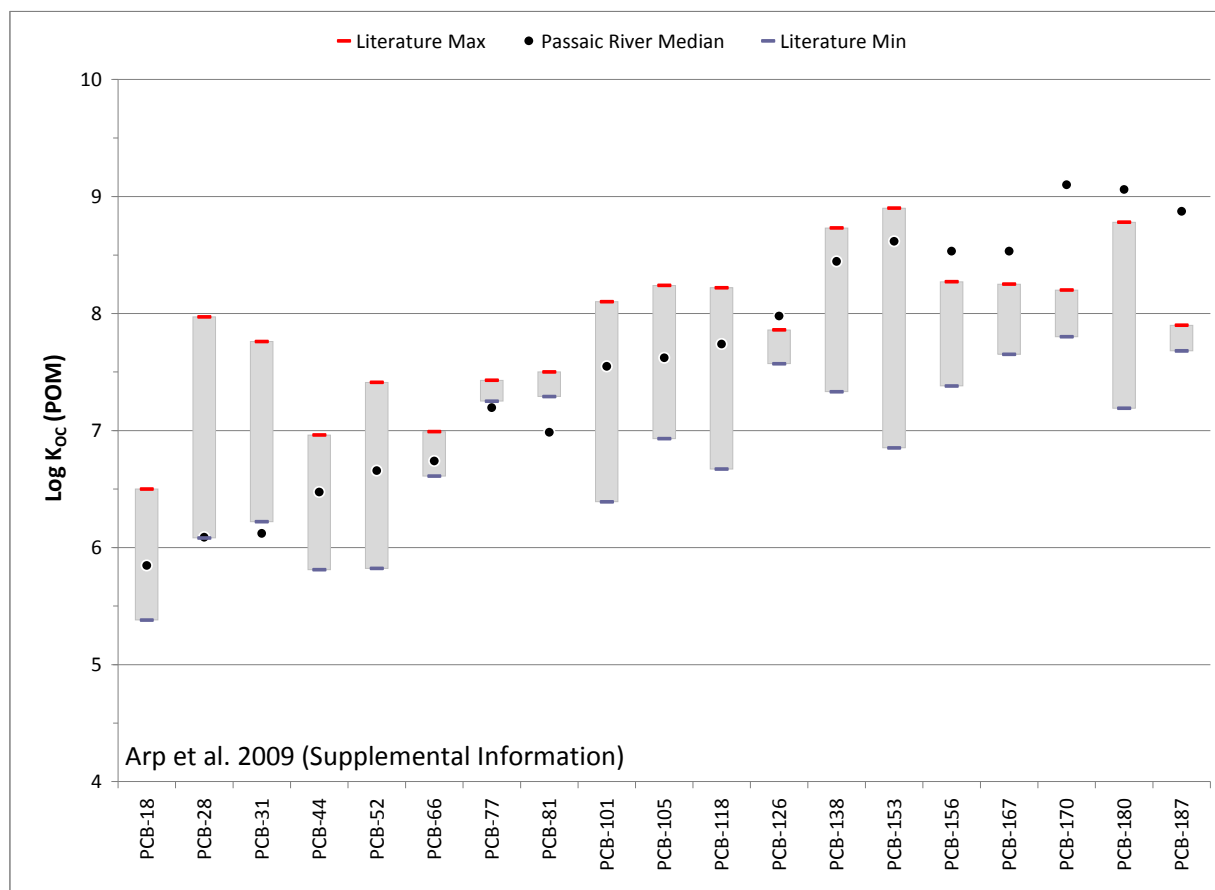


Figure 7. Comparison of K_{oc} (POM) of the LPR PCB Partitioning Study to the PCB Partition Coefficients Identified in Arp, et.al. 2009 [Common data were available for only 19 of the 42 congeners]

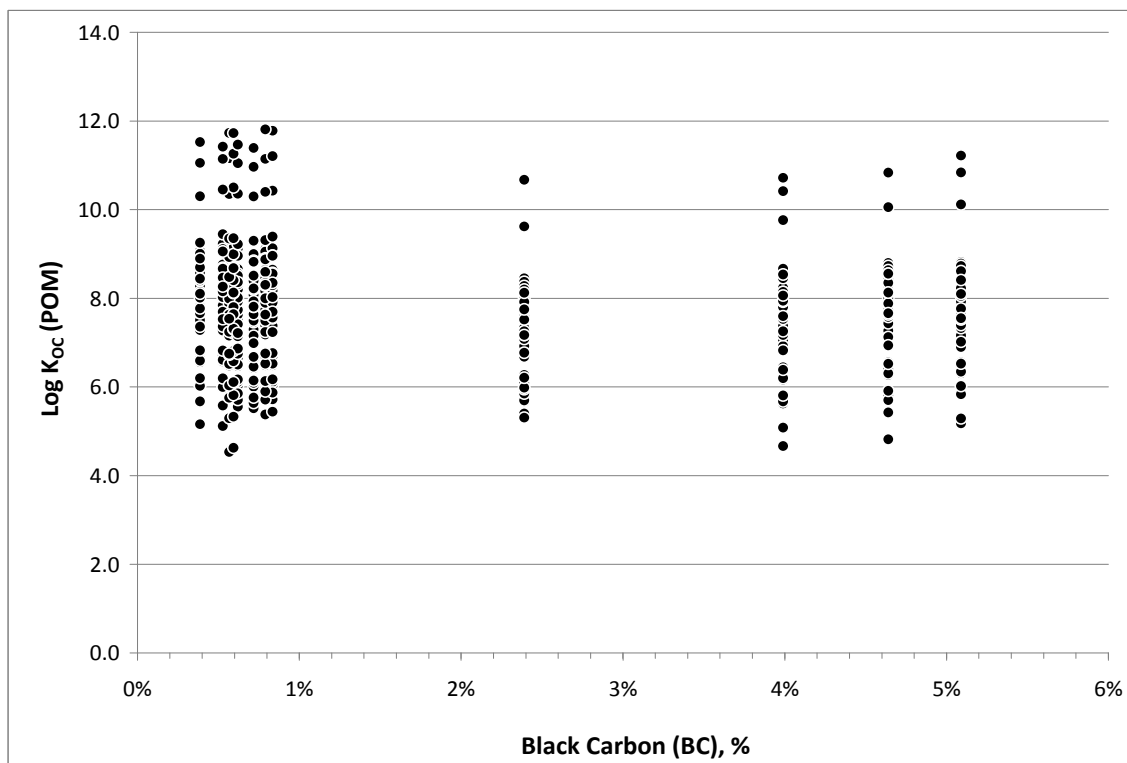
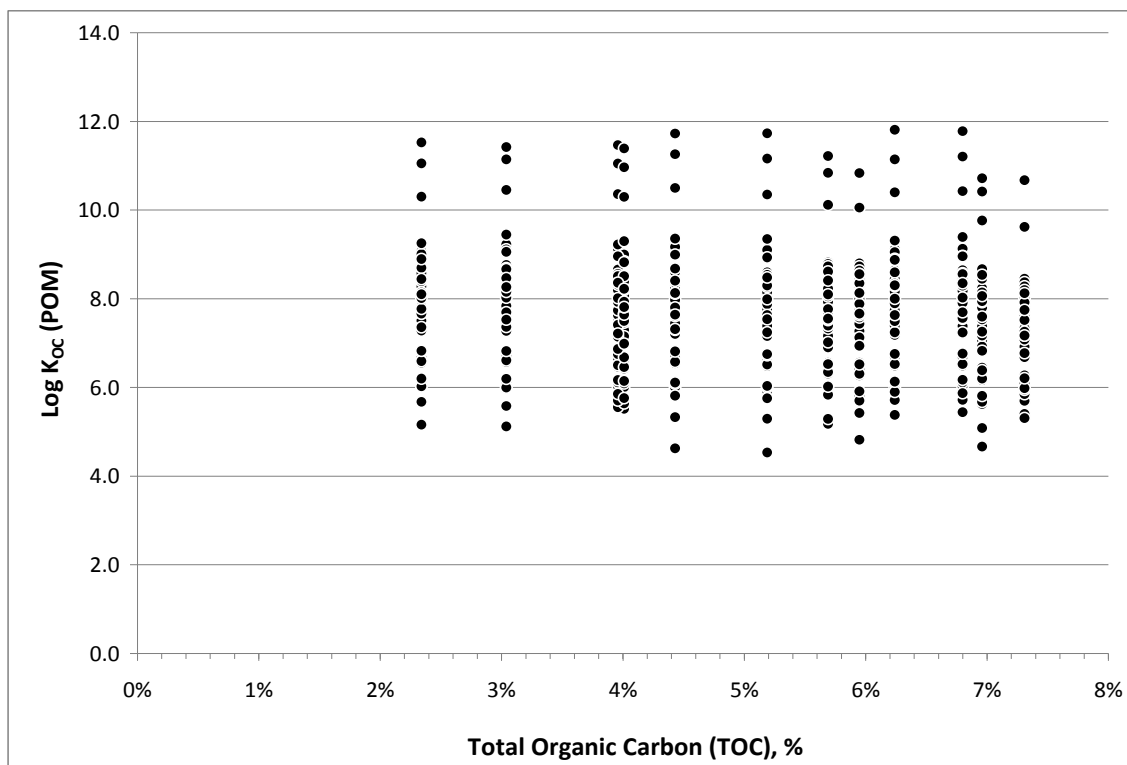


Figure 8. Log K_{oc} (POM)s for LPR sediments versus total and black carbon content of the sediment

Table 1
Surface Sediment Samples Selected for Study

Location ID	River Mile	Geomorphic Setting	Grain Size				Total Organic Carbon	Extractable Petroleum Hydrocarbons	Total PAHs (HMW+LMW)	Total PCBs
			Gravel	Sand	Silt	Clay				
			- % -				%	mg/Kg	mg/Kg	mg/Kg
CLRC-011	0.5	Point Bar	0	20	58	19	3.4	870	8.62	1.04
CLRC-015	1.1	Straight Side Channel	0.1	18	57	22	5.2	2,400	69.8	2.12
CLRC-044	7.0	Channel Bend Outer	1.7	28	36	35	5.3	975	36.4	1.28
CLRC-073	12.3	Point Bar	0	13	54	32	6.1	246	17.8	1.89
CLRC-079	13.6	Point Bar	11	84	2	3	18	1,100	412	0.536
CLRC-098	17.5	Dundee Lake	7.8	87	4.6	0.06	9.7	1,700	535	0.775

Table 2
PCB Congeners Selected for Analysis and their Properties

Selected Congener ^a	CASRN	Homologue Group	WHO List ^b	NOAA List ^c	Congener Coelution Note ^d	Octanol: Water Partitioning Coefficient Log (Kow) ^e		Aqueous Solubility Log (S) ^f	
						Mean	SD	Mean	SD
PCB1	2051-60-7	Mono				4.55	0.11	0.59	0.22
PCB8	34883-43-7	Di		X		5.10	0.30	-0.06	0.21
PCB18	37680-65-2	Tri		X	18, 30	5.50	0.24	-0.63	0.22
PCB20	38444-84-7	Tri			20, 28	5.56	0.12	-0.65	0.21
PCB28	7012-37-5	Tri		X	20, 29	5.63	0.09	-0.71	0.21
PCB30	35693-92-6	Tri			18, 30	5.48	0.11	-0.87	
PCB31	16606-02-3	Tri				5.66	0.12	-0.75	0.19
PCB44	41464-39-5	Tetra		X	44, 47, 65	5.93	0.21	-1.20	0.34
PCB47	2437-79-8	Tetra			44, 47, 65	6.05	0.21	-1.25	
PCB52	35693-99-3	Tetra		X		6.10	0.16	-1.40	0.31
PCB65	33284-54-7	Tetra			44, 47, 65	5.96	0.16	-1.56	
PCB66	32598-10-0	Tetra		X		6.09	0.27	-1.66	0.52
PCB77	32598-13-3	Tetra	X	X		6.37	0.30	-2.03	0.90
PCB81	70362-50-4	Tetra	X			6.27	0.21	-1.78	0.69
PCB90	68194-07-0	Penta			90, 101, 113	6.57	0.29	-1.97	0.20
PCB101	37680-73-2	Penta		X	90, 101, 113	6.72	0.28	-2.01	0.13
PCB105	32598-14-4	Penta	X	X		6.72	0.23	-2.21	0.40
PCB113	68194-10-5	Penta			90, 101, 113	6.44	0.21	-1.80	
PCB114	74472-37-0	Penta	X			6.70	0.27	-2.12	0.09
PCB118	31508-00-6	Penta	X	X		6.83	0.29	-2.26	0.21
PCB123	65510-44-3	Penta	X			6.72	0.27	-2.31	0.40
PCB126	57465-28-8	Penta	X	X		6.80	0.24	-2.46	0.65
PCB128	38380-07-3	Hexa		X	128, 166	7.19	0.33	-2.73	0.19
PCB129	55215-18-4	Hexa			129, 138, 157, 160	7.06	0.25	-2.72	
PCB138	35065-28-2	Hexa		X	129, 138, 157, 160	7.32	0.27	-2.62	0.17
PCB153	35065-27-1	Hexa		X	153, 168	7.48	0.29	-2.78	0.11
PCB156	38380-08-4	Hexa	X		156, 157	7.33	0.30	-2.89	0.20
PCB157	69782-90-7	Hexa	X		156, 157	7.26	0.25	-3.03	0.43
PCB160	41411-62-5	Hexa			129, 138, 157, 160	6.82	0.31	-2.64	
PCB163	74472-44-9	Hexa			129, 138, 157, 160	7.17	0.28	-2.70	0.24
PCB166	41411-63-6	Hexa			128, 166	6.88	0.27	-3.15	
PCB167	52663-72-6	Hexa	X			7.37	0.33	-2.83	0.18
PCB168	59291-65-5	Hexa			153, 168	7.22	0.24	-2.67	0.18
PCB169	32774-16-6	Hexa	X			7.40	0.25	-3.24	0.95
PCB170	35065-30-6	Hepta		X		7.63	0.35	-3.45	0.09
PCB180	35065-29-3	Hepta		X	180, 193	7.64	0.41	-3.35	0.25
PCB187	52663-68-0	Hepta		X		7.55	0.43	-3.26	0.40
PCB189	39635-31-9	Hepta	X			7.80	0.43	-3.57	0.15
PCB193	69782-91-8	Hepta			180, 193	7.48	0.32	-3.30	
PCB194	35694-08-7	Octa				8.48	0.60	-4.00	0.18
PCB206	40186-72-9	Nona				8.86	0.53	-4.74	0.01
PCB209	2051-24-3	Deca				8.98	0.71	-5.03	0.72

^a Congener ID based on BZ number. (Ballschmiter and Zell, 1980)

^b Congeners designated by the World Health Organization as having "dioxin-like" toxicity. (Van den Berg, 2006)

^c Congeners that are recommended by National Oceanic and Atmospheric Administration and USEPA for summing to determine total PCB concentrations (USEPA 1995).

^d Congeners that coelute during this analytical testing program

^e Mean and standard deviation of Log10 Kow values (modeled and predicted) as provided by Eisler and Belisle (1996), Jantschi and Bolboaca (2006), Paasivirta, and Sinkkonen (2009), U.S. EPA (2009), and Hawker and Connell (1988).

^f Mean and standard deviation of Log S values (modeled and predicted) as provided by Paasivirta, and Sinkkonen (2009) and U.S. EPA (2009).

Table 3. Comparison of Calculated Porewater Concentrations Using LDPE and POM to Air-Bridge Measurements					
PCB Congener	Porewater Concentration, picograms per liter (pg/l)				
	Calculated Concentration Based on Results from Tumbled Polymer Experiments				Measured Results from Air Bridge Experiments
	LDPE		POM		
	Concentration	% of Air Bridge	Concentration	% of Air Bridge	
PCB 44	32	68.1	63	134.0	47
PCB 52	140	45.2	92	29.7	310
PCB 101	660	79.5	670	80.7	830
PCB 110	180	33.3	490	90.7	540
PCB 138	790	106.8	1500	202.7	740
PCB 149	1400	107.7	650	50.0	1300
PCB 151	530	120.5	100	22.7	440
PCB 180	320	100.0	-	-	320
Average		82.6		87.2	

Table 4. Kpom Estimations - LPR Study and Hawthorne, et al., 2009				
PCB ⁷	Log Kow	Log Kpom		% Difference Between Kpoms ⁸
		LPRSA	Hawthorne	
8	5.10	4.70	4.69	2.3
18	5.50	5.15	5.12	6.7
28	5.63	5.30	5.68	-139.9
31	5.66	5.33	5.51	-51.4
44	5.93	5.63	5.65	-4.7
47	6.05	5.77	5.59	33.9
52	6.10	5.82	5.65	32.4
66	6.09	5.81	6.08	-86.2
105	6.72	6.51	6.38	25.9
118	6.83	6.65 ⁹	6.32	53.2
128	7.19	7.04	6.35	79.6
138	7.32	7.19	6.50	79.6
153	7.48	7.37	6.64	81.4
156	7.33	7.20	6.59	75.4
170	7.63	7.53	6.54	89.8
180	7.64	7.54	6.67	86.5
187	7.55	7.44	6.44	90.0
194	8.48	8.48	7.18	95.0

⁷ Only those PCBs that were examined by both Hawthorne, et.al. and the LPR study are presented in this table. Since Hawthorne did not look at all of the 42 congeners that were examined as part of the LPR study, the entire suite of Kpoms that were generated in the LPR study is not shown in this table.

⁸ This is the percent difference between the actual values of Kpom and not the log values

⁹ The K(pom) values that are highlighted within the black box were not determined experimentally but were estimated based on the Log K(pom) versus Log Kow relationship that was generated using the experimental data of the LPR study: $\text{Log Kpom} = 1.118 \text{ Log Kow} - 0.995$.

Table 5. Comparison of Literature Values of Kpoms for Selected PCB Congeners with Log Kows Greater Than 6.5					
PCB Congener	Log Kow	Log Kpom			
		LPR Study^(a)	Hawthorne et. al. 2009	Cornelissen, et.al. 2008	Jonker and Hawthorne, 2011 (In Review)
118	6.83	6.65	6.32	6.32	6.40
138	7.32	7.19	6.50	6.27	6.54
153	7.48	7.37	6.64	6.40	- ^(b)
156	7.33	7.20	6.59	-	6.70
180	7.64	7.54	6.67	6.18	-

Notes: (a) Predicted value based on the relationship: $\text{Log Kpom} = 1.118\text{Log Kow} - 0.995$
(b) No data

Table 6. Measured Log Koc (pom) ¹⁰					
PCB	Number of Samples ¹¹		Log Koc		
	N	N*	Minimum	Median	Maximum
PCB1	12	0	4.54	5.17	5.55
PCB101	12	0	7.08	7.55	7.67
PCB105	12	0	7.17	7.62	7.76
PCB113	12	0	6.77	7.24	7.36
PCB114	12	0	7.18	7.55	7.80
PCB118	12	0	7.27	7.74	7.84
PCB123	12	0	7.15	7.64	7.77
PCB126	8	4	7.21	7.98	8.30
PCB128	12	0	7.87	8.34	8.50
PCB129	12	0	7.60	8.15	8.29
PCB138	12	0	7.89	8.44	8.58
PCB153	12	0	8.04	8.62	8.76
PCB156	12	0	8.00	8.53	8.69
PCB157	12	0	7.92	8.45	8.61
PCB160	12	0	7.34	7.89	8.03
PCB163	12	0	7.73	8.28	8.41
PCB166	12	0	7.52	7.99	8.16
PCB167	12	0	8.12	8.53	8.70
PCB168	12	0	7.75	8.32	8.47
PCB169	0	12	*	*	*
PCB170	12	0	8.45	9.10	9.22
PCB18	12	0	5.69	5.85	6.04
PCB180	12	0	8.37	9.06	9.23
PCB187	10	2	8.28	8.87	9.11
PCB189	8	4	9.22	9.33	9.45
PCB193	12	0	8.20	8.89	9.05
PCB194	12	0	9.62	10.33	10.50
PCB20	12	0	5.62	6.00	6.05
PCB206	12	0	10.42	11.05	11.26
PCB209	10	2	10.72	11.50	11.81
PCB28	12	0	5.71	6.09	6.13
PCB30	12	0	5.67	5.83	6.02
PCB31	12	0	5.81	6.12	6.20
PCB44	12	0	5.95	6.47	6.58
PCB47	12	0	6.08	6.61	6.71
PCB52	12	0	6.27	6.66	6.81
PCB65	12	0	5.98	6.51	6.61
PCB66	12	0	6.21	6.74	6.82
PCB77	12	0	6.68	7.19	7.31
PCB8	12	0	5.08	5.50	5.72
PCB81	5	7	6.75	6.99	7.53
PCB90	12	0	6.92	7.38	7.51

¹⁰ Koc as determined using K_{pom} to estimate the porewater concentration $[C_{fw-POM} = \frac{C_{POM}}{K_{POM}}]$ and the following equation: $Koc = [C_{sed}/(foc)] / C_{fw-POM}$, where C_{sed} is the concentration of the PCB in the sediment and f_{oc} is the fraction of total organic carbon of the sediment

¹¹ N = Total number of sediment samples where the PCB concentrations in all media were greater than the method detection limits. N* is the number of samples where the PCB concentration in either the sediment or POM were below the method detection limits.